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The Fluctuations of a Quantum Degenerate Bose-Einstein Gas

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The fluctuations of a quantum degenerate Bose-Einstein gas

1. Introduction

We quote two familiar theorems on fluctuations in the grand ensemble of Gibbs (R.H. Fowler, Statistical Mechanics, IInd Edn. 1936):

$$\langle (\langle n \rangle - n)^2 \rangle = kT \partial \langle n \rangle / \partial \mu \quad (1)$$

$$\langle (\langle p \rangle - p)^2 \rangle = kT \left\{ \partial \langle p \rangle / \partial V - \langle \partial p / \partial V \rangle \right\} \quad (2)$$

where $\langle n \rangle$ and $\langle p \rangle$ are the mean density and mean pressure of a given phase in the ensemble, μ is the Gibbs free energy per particle and V the volume of the phase. Eq.(1) can also be expressed in the form

$$\langle (\Delta p / p)^2 \rangle = - kT / \{ V^2 (\partial p / \partial V)_T \} \quad (3)$$

giving the mean square relative density fluctuations of the phase. The step from Eq.(1) to Eq.(3) is valid only if $\partial p / \partial V$ is not zero; the infinity given then by Eq.(3) being spurious.

In an ideal Bose-Einstein gas we have

$$kT \partial \langle n \rangle / \partial \mu = V (2\pi m kT / h^2)^{3/2} \sum_j (1/j^{3/2}) e^{j\mu/kT} \quad (4)$$

and in terms of the degeneracy temperature T_0 defined by $\mu = 0$, or by

$$\langle n \rangle = V (2\pi m kT_0 / h^2)^{3/2} \sum_j (1/j^{3/2}) \quad (5)$$

we have

$$kT \partial \langle n \rangle / \partial \mu = \langle n \rangle (1/2.612) (T/T_0)^{3/2} \sum_j (1/j^{3/2}) e^{j\mu/kT} \quad (6)$$

When $T \rightarrow T_0$ and $\mu \rightarrow 0$, the series diverges and the relative fluctuations become formally infinite. In fact $\partial p / \partial V$ becomes zero here and the Eq.(3) ceases to be valid so this infinity is spurious.

2. Reciprocal relation between fluctuations at the degeneracy temperature

Consider an assembly of one phase only, but divide this phase into a large number of equal imaginary cells, each containing a large number of atoms. Every assembly in the ensemble is provided with exactly the same geometrical pattern of cells. The formalism of the grand ensemble carries over without material change to this arrangement if for the word "phase" one now substitutes the word "cell". Eq.(3) now reads to give the mean relative square fluctuations in density of one particular cell averaged over the ensemble, and the pressure derivative on the right is the average over the ensemble of the pressure derivative for a particular cell. To obtain a relation dealing directly with observed quantities for the phase as a whole, it is necessary to average once again over all the cells in the assembly. We may write this formally as

$$\langle\langle(\Delta \rho/\rho)^2\rangle\rangle = -kT/\{V^2\langle\partial\langle\rho\rangle/\partial V\rangle\} \quad (7)$$

This is the average over the assembly of the mean square fluctuations in the density of any one cell; but on the right side is the average over the assembly of the pressure derivative in a cell, and this is not what one would measure for the pressure derivative that vanishes at the degeneracy temperature. To repeat: the derivative that vanishes at the degeneracy temperature is the derivative of the mean pressure of the whole assembly which would be written $\partial\langle\langle\rho\rangle\rangle/\partial V$.

On this cell picture we also have to re-interpret Eq.(2) for the pressure fluctuations. To do this let us first average the cell pressures over the whole assembly, writing this $\langle\rho\rangle$, and then average over the ensemble, applying Eq.(2) to $\langle\rho\rangle$ instead of ρ :

$$\langle(\langle\langle\rho\rangle\rangle - \langle\rho\rangle)^2\rangle = kT\{\partial\langle\langle\rho\rangle\rangle/\partial V - \langle\partial\langle\rho\rangle/\partial V\rangle\} \quad (8)$$

The left hand side is now exactly what one would observe for the mean square fluctuations of the assembly pressure, and the right hand side contains both the observed pressure coefficient, and the pressure coefficient that appears in the relative density fluctuations in Eq.(7). Putting the observed pressure coefficient zero for the condition at the degeneracy temperature, using Eq.(8) in Eq.(7) we find the following reciprocal relation between the relative mean square fluctuations of density and pressure:

$$T = T_0: \quad \langle (\Delta \rho / \rho)^2 \rangle \langle (\Delta p / p)^2 \rangle = (kT/pV)^2 \quad (9)$$

The pressure here refers to the mean value for the assembly while the density refers to the cell, and the volume V is the volume of a cell. The density fluctuations cannot become infinite unless the pressure fluctuations vanish.

The pressure derivative of the Bose-Einstein gas remains zero for all $T < T_0$, and therefore Eq.(9) is valid below the degeneracy temperature and we may write:

$$T \leq T_0: \quad \langle (\Delta \rho / \rho)^2 \rangle \langle (\Delta p / p)^2 \rangle = (3.8/N^2)(T_0/T)^3 \quad (10)$$

where the density fluctuations refer to cells containing N atoms, and the pressure is that of the whole assembly. The magnitude of the fluctuations therefore increases with decreasing T , approaching infinity only when T approaches absolute zero.

3. Fluctuations at the Van der Waals critical point

Eq.(9) applies equally well to the fluctuations of a classical gas at the Van der Waals critical point, where the right hand side becomes roughly equal to $10/N^2$, where N is the number of atoms per cell. For an order of magnitude check on the relation, we may assume that the pressure and density on the left

are related by the Van der Waals equation in the neighborhood of the critical point: $\partial^3 p / \partial V^3 = -9p_c / V_c^3$ and $\Delta p = (1/3!)(\partial^3 p / \partial V^3) \Delta V^3$ so that

$$\Delta p / p_c = (3/2)(\Delta \rho / \rho_c)^3 \quad (11)$$

If quite formally of course we equate these quantities $\Delta p / p_c$ and $\Delta \rho / \rho_c$ to the relative fluctuations, to get the order of magnitude we find Eq.(9) becomes

$$\langle (\Delta \rho / \rho_c)^2 \rangle = (128/27)^{1/4} N^{-1/2} \quad (12)$$

where N is the mean number in the cell. CO_2 has a critical density 0.460 g/cm^3 and interatomic distance 14.4\AA , so a cell containing 10^6 molecules would have linear dimensions about half a wavelength of blue light. From Eq.(12) the density of such a cell would fluctuate by about 4%, and this is possibly enough to account for critical opalescence.

4. Liquid helium?

It has been suggested that the existence of these large fluctuations at the degeneracy temperature of a Bose-Einstein gas ought to show up in liquid helium if the latter has a Bose-Einstein explanation. This suggestion does not hold up under examination, because the necessary condition for large fluctuations is the vanishing of the pressure coefficient, not the nature of the statistics; the pressure coefficient does not vanish in liquid helium at the λ point.

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